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## (54) PRODUCTION OF HYDROPHOBIC AEROGEL

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for providing a hydrophobic aerogel by which a process time can be shortened to improve the efficiency of productivity, and the amount of a used solvent can be minimized to reduce the production cost.

SOLUTION: An alkoxysilane compound is simultaneously hydrolyzed and polycondensed to prepare a gel compound, and the gel compound is subjected to a hydrophobizing treatment. The treated gel compound is supercritically dried to provide the objective hydrophobic aerogel. In this case, the gel compound is prepared in the presence of an alcohol, and the gel compound without washing the gel compound with a solvent and in a state of the gel compound including water is subjected to the hydrophobizing treatment in a hydrophobization-treating solution containing an organic silane compound having an alkyl group and an alkoxy group. The solvent included in the gel compound subjected to the hydrophobizing treatment is substituted with carbon dioxide, and the substituted gel compound is supercritically dried.

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CLAIMS

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[Claim(s)]

[Claim 1] While hydrolyzing an alkoxysilane compound, after carrying out condensation polymerization, preparing a gel compound and carrying out hydrophobing processing of this gel compound, by carrying out supercritical drying After preparing the above-mentioned gel compound under existence of alcohol in manufacturing hydrophobic aerogel and the gel compound has contained water, without washing a gel compound with a solvent Hydrophobing processing of this gel compound is carried out in the hydrophobing processing solution containing the organic silane compound which has an alkyl group and an alkoxyl group. Subsequently, the manufacture approach of the hydrophobic aerogel characterized by permuting the solvent contained in this gel compound that carried out hydrophobing processing by the carbon dioxide, and carrying out supercritical drying of the gel compound after this.

[Claim 2] The manufacture approach of the hydrophobic aerogel according to claim 1 characterized by carrying out supercritical drying of the gel compound, without washing a gel compound with a solvent after carrying out hydrophobing processing of the gel compound.

[Claim 3] After preparing a gel compound and carrying out hydrophobing processing of this gel compound by making a sodium silicate gel, by carrying out supercritical drying In manufacturing hydrophobic aerogel, hydrophobing processing is carried out in the hydrophobing processing solution containing the organic silane compound which has an alkyl group and an alkoxyl group for the above-mentioned gel compound. Next, the manufacture approach of the hydrophobic aerogel characterized by permuting the solvent contained in a gel compound by the carbon dioxide, and carrying out supercritical drying of the gel compound after this, without washing a gel compound with a solvent.

[Claim 4] The manufacture approach of the hydrophobic aerogel according to claim 1 to 3 characterized by setting the gel compound which carried out hydrophobing processing in a supercritical drying container, and carrying out supercritical drying of the gel compound, without being filled up with a solvent in a supercritical drying container.

[Claim 5] The manufacture approach of the hydrophobic aerogel according to claim 1 to 4 characterized by changing a hydrophobing processing solution into an acid condition, and carrying out hydrophobing processing of the gel compound under acid conditions.

[Claim 6] The manufacture approach of the hydrophobic aerogel according to claim 1 to 5 characterized by using dimethyldimethoxysilane as an organic silane compound.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] It is related with the manufacture approach of aerogel of the rate of optical refraction having been low, and having excelled in hydrophobicity while this invention was excellent in adiathermic and light transmission nature.

[0002]

[Description of the Prior Art] The silica aerogel useful as a heat insulator which has translucency is offered from the former. As a process of this aerogel, an ARUKOSHI xylan is hydrolyzed and the approach of drying the gel compound obtained by carrying out condensation polymerization of this on the supercritical conditions more than the critical point of this dispersion medium under existence of a dispersion medium is learned as indicated by the U.S. Pat. No. 4402927 official report, the U.S. Pat. No. 4432956 official report, and the U.S. Pat. No. 4610863 official report.

[0003] In these approaches, organic solvents, such as a carbon dioxide or ethanol, are used as a dispersion medium at the time of supercritical drying. However, the high silanol group of a hydrophilic property is formed of the moisture to which hygroscopicity was discovered since it had the silanol group on the front face, and it was easy to adsorb the moisture in an ambient atmosphere, and stuck further, the aerogel obtained by carrying out supercritical drying, using a carbon dioxide as a dispersion medium passes through the moisture in an ambient atmosphere, and it much more becomes easy to stick with the time to it. Moreover, about the aerogel obtained by carrying out supercritical drying, using organic solvents, such as ethanol, as a dispersion medium, since it has the alkoxyl group on the front face, although it has hydrophobicity immediately after supercritical drying, the moisture of an ambient atmosphere hydrolyzes with time, a silanol group is formed in that result table side, and this alkoxyl group comes to adsorb the moisture in an ambient atmosphere similarly.

[0004] And when aerogel adsorbed moisture in this way, it was what the problem that a property optical [ adiathermic / translucency, adiathermic, etc. / that ] and thermal will fall, and change and the crack of a dimension will arise with the contraction which originates in adsorption of this moisture further, will cause degradation of quality or the engine performance these results, and practicality will be missing generates.

[0005] Then, in order that this invention person etc. may conquer the fault by the water adsorption of this aerogel, After carrying out hydrophobing processing of the gel compound which obtained alkoxysilane and a sodium silicate as a raw material in a liquid solvent, by performing supercritical drying the approach (JP,5-279011,A —) of obtaining the aerogel made into hydrophobicity refer to Japanese Patent Application No. No. 342176 [ eight to ] — or by adding a hydrophobing processing agent in a supercritical drying container at the time of supercritical drying, and performing hydrophobing processing in the state of supercritical The approach (refer to JP,7-138375,A and Japanese Patent Application No. No. 343282 [ eight to ]) of obtaining the aerogel made into hydrophobicity is proposed. Thus, by carrying out hydrophobing processing of the aerogel, the aerogel in which a property does not deteriorate with time by adsorption of moisture can be obtained.

[0006] In carrying out hydrophobing processing of the gel compound as mentioned above, and manufacturing hydrophobic aerogel, he uses a solvent before hydrophobing processing and is trying to wash a gel compound beforehand conventionally here. This is for preventing the moisture contained in the gel compound after gelation reacting with a hydrophobing processing agent, and reducing the reaction effectiveness of a hydrophobing processing agent.

[0007] Moreover, in order to remove the reaction by-product generated by the hydrophobing processing agent which remains in a gel compound after hydrophobing processing, or hydrophobing processing, he uses a solvent similarly and is trying to wash a gel compound. If the concentration of the hexamethyldisilazane which remains in the gel compound after hydrophobing processing is more than solubility to the inside of the carbon dioxide of the dispersion medium of supercritical drying when hexamethyldisilazane is used as for example, a hydrophobing processing agent, this In the supercritical drying process after hydrophobing processing, a gas-liquid interface arises within a desiccation container. The problem that the structure of a gel compound will be destroyed as a result arises, or Or it is for preventing that the problem that an ammonium carbonate deposits [ the ammonia generated as a reaction by-product by hydrophobing processing ] in response to the time of supercritical drying with a carbon dioxide, and this blocks piping of supercritical drying equipment arises.

[0008] Moreover, in case the gel compound which carried out hydrophobing processing is set in a desiccation container in a supercritical drying process, he is trying to fill up solvents, such as alcohol, with the manufacturing method of conventional hydrophobic aerogel beforehand in a desiccation container. In case this sets a gel compound in a desiccation container, it is for preventing a gel compound's drying and a crack occurring.

[0009]

[Problem(s) to be Solved by the Invention] As mentioned above, while the manufacturing method of conventional hydrophobic aerogel took the process time amount of washing since a solvent was used for a hydrophobing processing front and the back for a gel compound and he was trying to wash, and productive efficiency became very low, it was what the amount of the solvent used becomes great and has a problem also in respect of a production cost. Moreover, since it is filled up with a solvent in the container of supercritical drying and he is trying to set a gel compound If it has a problem in the production cost by use of a solvent, it is filled up with a solvent in a supercritical drying container still in this way and a gel compound is set while the injection time of a solvent is required similarly and productive efficiency becomes low Since it filled up with the solvent also around the gel compound in the supercritical drying container, the time amount taken to permute the solvent in a supercritical drying container with a carbon dioxide at the time of supercritical drying became long, and productive efficiency was what becomes still lower.

[0010] It aims at offering the manufacture approach of the hydrophobic aerogel which this invention is made in view of the above-mentioned point, and can shorten process time amount, and can raise the effectiveness of productivity, and can minimum-ize the amount of the solvent used, and can make a production cost cheap.

[0011]

[Means for Solving the Problem] The manufacture approach of the hydrophobic aerogel concerning claim 1 of this invention While hydrolyzing an alkoxysilane compound, after carrying out condensation polymerization, preparing a gel compound and carrying out hydrophobing processing of this gel compound, by carrying out supercritical drying After preparing the above-mentioned gel compound under existence of alcohol in manufacturing hydrophobic aerogel and the gel compound has contained water, without washing a gel compound with a solvent Hydrophobing processing of this gel compound is carried out in the hydrophobing processing solution containing the organic silane compound which has an alkyl group and an alkoxyl group. Subsequently, the solvent contained in this gel compound that carried out hydrophobing processing is permuted by the carbon dioxide, and it is characterized by carrying out supercritical drying of the gel compound after this.

[0012] Moreover, invention of claim 2 is characterized by carrying out supercritical drying of the gel compound in above-mentioned claim 1, without washing a gel compound with a solvent, after carrying out hydrophobing processing of the gel compound.

[0013] The manufacture approach of the hydrophobic aerogel concerning claim 3 of this invention After preparing a gel compound and carrying out hydrophobing processing of this gel compound by making a sodium silicate gel, by carrying out supercritical drying In manufacturing hydrophobic aerogel, hydrophobing processing is carried out in the hydrophobing processing solution containing the organic silane compound which has an alkyl group and an alkoxy group for the above-mentioned gel compound. Next, without washing a gel compound with a solvent, the solvent contained in a gel compound is permuted by the carbon dioxide, and it is characterized by carrying out supercritical drying of the gel compound after this.

[0014] Moreover, in above-mentioned claim 1 thru/or 3, without being filled up with a solvent in a supercritical drying container, invention of claim 4 sets the gel compound which carried out hydrophobing processing in a supercritical drying container, and is characterized by carrying out supercritical drying of the gel compound.

[0015] Moreover, invention of claim 5 is characterized by changing a hydrophobing processing solution into an acid condition, and carrying out hydrophobing processing of the gel compound under acid conditions in above-mentioned claim 1 thru/or 4.

[0016] Moreover, invention of claim 6 is characterized by using dimethyldimethoxysilane as an organic silane compound in above-mentioned claim 1 thru/or 5.

[0017]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained.

[0018] Generally as a silica raw material for obtaining aerogel, alkoxy silane and a sodium silicate (water glass) are used. As alkoxy silane, 2 organic-functions alkoxy silane, 3 organic-functions alkoxy silane, There is 4 organic-functions alkoxy silane. As 2 organic-functions alkoxy silane Dimethyldimethoxysilane, Dimethyl diethoxysilane, diphenyl diethoxysilane, diphenyldimethoxysilane, Methylphenyl diethoxysilane, methylphenyl dimethoxysilane, As 3 organic-functions alkoxy silane, diethyldiethoxysilane, diethyldimethoxysilane, etc. Methyl trimethoxysilane, Methyl triethoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, Phenyltrimethoxysilane, a phenyl TORIETOSHI xylan, etc. can be mentioned for a tetramethoxy silane, a tetra-ethoxy silane, etc. as 4 organic-functions alkoxy silane, respectively.

[0019] And by mixing with the solvent which has compatibility for this alkoxy silane in water and water, and dissolves alkoxy silane, and mixing this mixed solution, hydrolysis and condensation polymerization advance and a gel compound can be obtained. By this invention, alcohol, such as a methanol, ethanol, isopropanol, and a butanol, is used as this solvent.

[0020] Moreover, about a sodium silicate, a gel compound can be obtained by making a solution into a supersaturation condition, depositing a silicon oxide, and making it gel by adjusting pH of a sodium-silicate solution (water glass solution) near neutrality.

[0021] Next, hydrophobing down stream processing which carries out hydrophobing of the gel compound prepared as mentioned above is explained. Hydrophobing processing is performed in order to make the hydroxyl group of the silanol group which a gel compound has react with the functional group which a hydrophobing processing agent has and to carry out hydrophobing. Although especially the technique of performing hydrophobing processing is not limited, after being immersed, agitating a gel compound for example, in the hydrophobing processing solution made to dissolve a hydrophobing processing agent in a solvent and making a hydrophobing processing agent permeate in a gel compound, it heats if needed, and the method of making a hydrophobing processing reaction perform is mentioned.

[0022] While dissolving easily using the organic silane compound which has an alkyl group and an alkoxy group as a hydrophobing processing agent in this invention here into the carbon dioxide used as a solvent in the case of supercritical drying, it is desirable to use what also dissolves the by-product produced in the case of a hydrophobing processing reaction into a carbon dioxide. As such a hydrophobing processing agent, trimethylmethoxysilane, dimethyldimethoxysilane, methyl trimethoxysilane, ethyltrimethoxysilane, trimethylethoxysilane, dimethyl diethoxysilane, methyl triethoxysilane, etc. can be mentioned, for example.

[0023] Thus, when it consists of an alkyl group and an alkoxy group and moisture exists in the gel compound before hydrophobing processing, a hydrophobing processing agent is hydrolyzed, an alkoxy group replaces a hydroxyl group and a hydrophobing processing agent becomes easy

to react with the hydroxyl group on the front face of pore of a gel compound. Although the above-mentioned hydrophobing processing agent has low reactivity compared with the hexamethyldisilazane generally used as a hydrophobing processing agent, when moisture exists in a gel compound, reactivity increases.

[0024] Here, when a sodium silicate is used as a silica raw material, the gel compound after gelation is obtained in the state of the condition, i.e., a hydrogel, that the interior is filled up with water. Since the above-mentioned hydrophobing processing agent cannot melt into water easily, it is desirable that solvents, such as water and alcohol made to dissolve a hydrophobing processing agent mutually, wash a gel compound in advance of hydrophobing processing in this case.

[0025] As a solvent, on the other hand, since gelation was processed for alcohol when alkoxysilane was used as a silica raw material, the interior of a gel compound will be able to be filled up with alcohol with water, and water and a hydrophobing processing agent can be dissolved in this alcohol. Therefore, when it is made to gel in alcohol, using alkoxysilane as a silica raw material, although a solvent washes a gel compound, it is unnecessary, and hydrophobing processing can be performed in the condition [ that moisture has been included in the gel compound ].

[0026] Moreover, an acid is added, it changes into an acid condition, and you may make it raise the reactivity of a hydrophobing processing agent under acid conditions into a hydrophobing processing solution in this hydrophobing down stream processing. It is desirable to change into an acid condition as [ become / a pH value / as an acid to add, can mention organic acids, such as inorganic acids, such as a hydrochloric acid and a sulfuric acid, and an acetic acid, oxalic acid, here, and / the range of 4-6 ].

[0027] As a solvent used in order to dissolve the above-mentioned hydrophobing processing agent, with the solvent which a hydrophobing processing agent dissolves easily and the gel compound before hydrophobing processing contains although alcohols, such as a methanol, ethanol, and isopropanol, a xylene, toluene, benzene, N.N-dimethylformamide, etc. can be mentioned, if replaceable, it will not be limited to these things, for example.

[0028] Next, the process which carries out supercritical drying of the gel compound which performed hydrophobing processing as mentioned above is explained. Supercritical drying is the drying method for removing a solvent (dispersion medium) from the critical point or the critical point of a solvent included in the gel compound gradually in the supercritical ambient atmosphere of elevated-temperature high pressure. Although there is also the approach of drying under these supercritical conditions using a methanol, ethanol, etc. as this solvent, since critical temperature is very high in this case, from fields, such as safety, to carrying out industrially, it is not desirable. For this reason, he is trying to use a carbon dioxide with critical temperature low as a solvent (dispersion medium) in this invention.

[0029] And after permuting all or some of solvents with which it is immersed into the liquefaction carbon dioxide of 50 - 60 atmospheric-pressure extent, and a gel compound contains a gel compound, for example by the liquefaction carbon dioxide with the critical point lower than this solvent in carrying out supercritical drying of the gel compound which performed the above-mentioned hydrophobing processing in this invention, it can dry under the supercritical conditions of the independent system of a carbon dioxide, or the mixed stock of a carbon dioxide and a solvent.

[0030] Here, in order to be easy to dissolve in a supercritical carbon dioxide and to dissolve in infinity in a supercritical drying process above predetermined temperature and a flow and pressure requirement further, a gas-liquid interface does not generate the above-mentioned hydrophobing processing agent used in this invention within a supercritical drying container. And at the hydrophobing processing reaction using the above-mentioned hydrophobing processing agent, since the reaction by-product generated is also alcohol, it dissolves in a supercritical carbon dioxide similarly. Even if it skips the process which washes the gel compound after hydrophobing processing with a solvent, the hydrophobing processing agent or reaction by-product which remain in a gel compound do not have a bad influence on a gel compound at the time of supercritical drying, and it becomes unnecessary therefore, for a solvent to wash the gel

compound after hydrophobing processing.

[0031] Moreover, in setting a gel compound in a supercritical drying container, in a supercritical drying process, a gel compound can be set in the condition of not being beforehand filled up with the solvent in a supercritical drying container. In this case, although there is a possibility that a crack may occur by desiccation of a gel compound, when it is not necessary to make an issue of debasement especially by generating of a crack, it may be made to set a gel compound in the condition of not being beforehand filled up with the solvent in a supercritical drying container. Therefore, the need that a lot of solvents and carbon dioxides in a supercritical drying container are permuted at the time of supercritical drying is lost like [ in the case of being filled up with a solvent in a supercritical drying container, and setting a gel compound ], a gel compound is only set in a supercritical drying container, supercritical drying can be performed, and supercritical drying can be performed efficiently.

[0032] In addition, although not limited especially about the configuration of the gel compound with which hydrophobing processing and supercritical drying are presented, since the drying efficiency of a gel compound can be raised and particle size of a gel compound can be made [ and ] small by carrying out like [ thing / tabular ] the shape of a bead, or the letter of grinding, it is much more hard coming to generate the crack by the desiccation at the time of setting a gel compound in a supercritical drying container.

[0033] By carrying out hydrophobing processing and carrying out supercritical drying of the gel compound further as mentioned above, the outstanding hydrophobicity is given and the silica aerogel which has high translucency can be obtained. That is, the hydroxyl group of the silanol group which exists in the silica front face of aerogel is permuted by hydrophobing processing by the hydrophobic group of a hydrophobing processing agent, adsorbing the moisture in an ambient atmosphere of the aerogel obtained is lost, and the fall of the property with time by water absorption of it is lost. And in case it can dry without the phase transition of the solvent in a gel compound, i.e., the so-called evaporation and condensation, happening and a solvent is removed by supercritical drying, it can control the structure of a gel compound being destroyed or condensing, and the aerogel obtained by supercritical drying will become porosity. And this aerogel is the structure which consists of a very detailed silica particle, and as for that particle diameter, far smaller than the wavelength of light, although its space between particles is smaller [ than the mean free path of air ] uniform, and its thermal conductivity is small and it is a porous body, it has translucency.

[0034] The aerogel concerning this invention obtained as mentioned above is useful for applications, such as a heat insulator in opening, an acoustic material, the Cherenkov component, and catalyst support.

[0035]

[Example] Next, an example explains this invention concretely.

[0036] (Example 1) After slushing into the container the sol obtained by blending 47 weight sections and a methanol in the 163 weight sections, blending 50 weight sections and 15-N aqueous ammonia for water at a rate of 1 weight section, and agitating the oligomer (the "methyl silicate 51" by COL coat incorporated company, average molecular weight 470 [ about ]) of a tetramethoxy run for about 30 seconds and making this sol gel, it was left at the room temperature on the 1st, and the gel compound was obtained. Thus, the obtained gel compound was ground and the particle whose mean particle diameter is about 3mm was produced.

[0037] Next, as a hydrophobing processing solution, the isopropanol solution of the dimethyldimethoxysilane (reagent by Dow Corning Toray Silicone, Inc.) of 0.6 mol/L was prepared, and concentration was immersed in this hydrophobing processing solution in the gel compound of the shape of a particle produced as mentioned above, and performed hydrophobing processing for three days at the room temperature. At this time, it set up so that the volume of a hydrophobing processing solution and the volume of a gel compound might become equal, and the hydrophobing processing solution was agitated several times on the 1st.

[0038] Next, hydrophobic aerogel was obtained by putting the gel compound which carried out hydrophobing processing in this way into a supercritical container, making the inside of a supercritical drying container into 80 degrees C and 160 atmospheric pressures which are the



supercritical conditions of a carbon dioxide, using a carbon dioxide as a solvent (dispersion medium), and performing supercritical drying for 5 hours.

[0039] (Example 2) In the example 1, the methanol was used instead of isopropanol as a solvent for dissolving a hydrophobing processing agent, and the hydrophobing processing solution was prepared. Others obtained hydrophobic aerogel like the example 1.

[0040] (Example 3) In the example 1, into the hydrophobing processing solution, it adds 2% and dilute hydrochloric acid was used by the volume. Others obtained hydrophobic aerogel like the example 1.

[0041] (Example 4) In the example 1, methyl trimetoxysilane (reagent by Dow Corning Toray Silicone, Inc.) was used instead of dimethyldimethoxysilane as a hydrophobing processing agent, and the hydrophobing processing solution was prepared. Others obtained hydrophobic aerogel like the example 1.

[0042] (Example 5) In setting the gel compound which performed hydrophobing processing in a supercritical drying container, in the example 1, it was beforehand filled up with isopropanol in the supercritical drying container. Others obtained hydrophobic aerogel like the example 1.

[0043] (Example 6) The inside of the column with which ion-exchange resin ("Amberlite IR-120B" by ORGANO CORP.) was filled up with the hydrosol solution which mixed the sodium-silicate water solution (the "J sodium silicate No. 3" by Nippon Chemical Industrial Co., Ltd.) in 10 weight sections, mixed ion exchange water at a rate of 32 weight sections, and was prepared was passed. At this time, the ratio of the number of mols of the sodium atom in a hydrosol solution and the exchangeable number of mols of ion exchange resin was 0.5. Moreover, pH of the hydrosol solution obtained by passing ion exchange resin was 3. Next, 1 weight section addition of the aqueous ammonia of concentration was carried out 2.8% of the weight at this hydrosol solution 200 weight section, and it agitated quickly. pH of the hydrosol solution at this time was 6. This hydrosol solution was put at the room temperature on the 1st, and the hydrogel was obtained. The obtained gel compound was ground and the particle whose mean particle diameter is 3mm was produced.

[0044] It was immersed in the isopropanol of this volume and the particle of the obtained gel compound was permuted by the water in a gel compound. This permutation actuation was performed a total of 4 times. And the rest carried out hydrophobing processing like the example 1, carried out supercritical drying further, and obtained hydrophobic aerogel.

[0045] (Example 1 of a comparison) In the example 1, before carrying out hydrophobing processing, isopropanol was used, the gel compound was washed twice, and also after hydrophobing processing, isopropanol was used and the gel compound was washed twice. Others obtained hydrophobic aerogel like the example 1. At this time, washing of a gel compound required the day per washing.

[0046] (Example 2 of a comparison) In the example 1 of a comparison, hexamethyldisilazane (reagent by Dow Corning Toray Silicone, Inc.) was used instead of dimethyldimethoxysilane as a hydrophobing processing agent, and the hydrophobing processing solution was prepared. Others obtained hydrophobic aerogel like the example 1 of a comparison.

[0047] (Example 3 of a comparison) In the example 1, hexamethyldisilazane (reagent by Dow Corning Toray Silicone, Inc.) was used instead of dimethyldimethoxysilane as a hydrophobing processing agent, and the hydrophobing processing solution was prepared. Others obtained hydrophobic aerogel like the example 1.

[0048] (Example 4 of a comparison) In the example 1, it was made not to perform hydrophobing processing and aerogel was obtained like the example 1.

[0049] The silica raw material in above-mentioned examples 1-6 and examples 1-4 of a comparison, the class of hydrophobing processing agent, The class of solvent of a hydrophobing processing solution, pH of a hydrophobing processing solution, the bath ratio of a gel compound and a hydrophobing processing solution, The days which the existence of restoration of the solvent to the count of washing before hydrophobing processing, the count of washing after hydrophobing processing, and the supercritical drying container in the case of supercritical drying and the amount of the solvent used per 1l. of gel compounds, and hydrophobing down stream processing took are shown in Table 1.

[0050]

[Table 1]

	silica 原料	疎水化処理剤	溶媒	処理液 のpH	ゲルと溶液 の溶比	疎水化前 洗浄回数	疎水化後 洗浄回数	超臨界乾燥 時の溶媒 充填の有無	ゲル当り の溶媒 使用量	疎水化 処理工程 日数 (日)
実施例1	メチルケート51	ジメチルジメトキシシラン	イソプロパノール	7	0.5	0	0	なし	1	3
実施例2	メチルケート51	ジメチルジメトキシシラン	メタノール	7	0.5	0	0	なし	1	3
実施例3	メチルケート51	ジメチルジメトキシシラン	イソプロパノール	5	0.5	0	0	なし	1	3
実施例4	メチルケート51	メチルトリメトキシシラン	イソプロパノール	7	0.5	0	0	なし	1	3
実施例5	メチルケート51	ジメチルジメトキシシラン	イソプロパノール	7	0.5	0	0	あり	2	3
実施例6	ケイ酸ソーダ	ジメチルジメトキシシラン	イソプロパノール	7	0.5	4	0	なし	5	3
比較例1	メチルケート51	ジメチルジメトキシシラン	イソプロパノール	7	0.5	2	2	あり	6	7
比較例2	メチルケート51	ヘキサメチルジシラザン	イソプロパノール	7	0.5	2	2	あり	6	7
比較例3	メチルケート51	ヘキサメチルジシラザン	イソプロパノール	7	0.5	0	0	なし	1	3
比較例4	メチルケート51	—	—	—	—	0	0	なし	0	0

[0051] Next, the bulk density of aerogel after the humidity resistance test which exposes aerogel immediately after supercritical drying for 48 hours into the ambient atmosphere of the

temperature of 60 degrees C and 90% of humidity RH, thermal conductivity, and light transmittance were measured about the aerogel obtained as mentioned above in examples 1-5 and the examples 1-4 of a comparison. The thermal conductivity measuring apparatus by the stationary method by Hidehiro energy machine incorporated company was used for thermal conductivity here, and it is an approach based on ASTM-C518, and measured on the laying temperature of 20 degrees C, and 40-degree C conditions. Moreover, about light transmittance, it asked by measuring the illuminance before and behind installation of the sample produced in thickness of 12mm by aerogel by making a fluorescent lamp into the light source all over the acrylic box using an illuminometer (illuminometer by YOKOGAWA instrument incorporated company "a part number 510-02"). These results are shown in Table 2.

[0052]

[Table 2]

	かさ密度 ( $\text{g/cm}^3$ )		熱伝導率 ( $\text{W/mK}$ )		光透過率 (%)	
	超臨界乾燥後	耐湿試験後	超臨界乾燥後	耐湿試験後	超臨界乾燥後	耐湿試験後
実施例1	0.11	0.11	0.019	0.020	86	86
実施例2	0.12	0.12	0.020	0.020	85	85
実施例3	0.12	0.12	0.019	0.019	84	84
実施例4	0.12	0.13	0.020	0.020	85	86
実施例5	0.11	0.11	0.020	0.021	87	86
実施例6	0.11	0.12	0.020	0.021	83	84
比較例1	0.11	0.12	0.020	0.021	87	85
比較例2	0.12	0.12	0.019	0.019	86	86
比較例3	0.14	0.15	0.021	0.022	73	70
比較例4	0.11	0.37	0.020	0.350	87	38

[0053] It is checked that the example 6 which does not perform washing after the examples 1-5 which do not perform washing hydrophobing processing before or after hydrophobing processing, and hydrophobing processing also has damp-proof ability equivalent to the thing of the examples 1 and 2 of a comparison which performs washing hydrophobing processing before and after hydrophobing processing so that it may see in Table 2.

[0054]

[Effect of the Invention] The manufacture approach of the hydrophobic aerogel which starts claim 1 of this invention as mentioned above While hydrolyzing an alkoxysilane compound, after carrying out condensation polymerization, preparing a gel compound and carrying out hydrophobing processing of this gel compound, by carrying out supercritical drying After

preparing the above-mentioned gel compound under existence of alcohol in manufacturing hydrophobic aerogel and the gel compound has contained water, without washing a gel compound with a solvent Hydrophobing processing of this gel compound is carried out in the hydrophobing processing solution containing the organic silane compound which has an alkyl group and an alkoxy group. Subsequently, since the solvent contained in this gel compound that carried out hydrophobing processing is permuted by the carbon dioxide and it was made to carry out supercritical drying of the gel compound after this Alcohol is contained in the gel compound of an alkoxy silane compound. It is what can be made to be able to dissolve water and a hydrophobing processing agent in this alcohol, and can perform hydrophobing processing. And the hydrophobing processing agent which consists of an organic silane compound which has an alkyl group and an alkoxy group Will hydrolyze, if moisture exists in a gel compound, and an alkoxy group replaces a hydroxyl group. It is what becomes easy to react with the hydroxyl group on the front face of pore of a gel compound, and can carry out hydrophobing processing of the gel compound. Consequently, a solvent does not need to wash a gel compound and hydrophobing processing can be performed in the condition [ that moisture has been included in the gel compound ]. While the process which washes a gel compound with a solvent can become unnecessary, can shorten process time amount and can raise the effectiveness of productivity, the amount of the solvent used can be minimum-ized and a production cost can be made cheap. [0055] Moreover, since invention of claim 2 was made to carry out supercritical drying of the gel compound in above-mentioned claim 1, without washing a gel compound with a solvent after carrying out hydrophobing processing of the gel compound While it is easy to dissolve the above-mentioned hydrophobing processing agent in a supercritical carbon dioxide and a gas-liquid interface does not occur within a supercritical drying container And the reaction by-product generated at the hydrophobing processing reaction using the above-mentioned hydrophobing processing agent is alcohol, and is what is similarly dissolved in a supercritical carbon dioxide. Without it seeming that the hydrophobing processing agent and reaction by-product which remain in a gel compound have a bad influence on a gel compound at the time of supercritical drying While being able to skip the process which washes the gel compound after hydrophobing processing with a solvent, being able to shorten process time amount and being able to raise the effectiveness of productivity, the amount of the solvent used can be minimum-ized and a production cost can be made cheap.

[0056] The manufacture approach of the hydrophobic aerogel concerning claim 3 of this invention After preparing a gel compound and carrying out hydrophobing processing of this gel compound by making a sodium silicate gel, by carrying out supercritical drying In manufacturing hydrophobic aerogel, hydrophobing processing is carried out in the hydrophobing processing solution containing the organic silane compound which has an alkyl group and an alkoxy group for the above-mentioned gel compound. Next, since the solvent contained in a gel compound is permuted by the carbon dioxide and it was made to carry out supercritical drying of the gel compound after this, without washing a gel compound with a solvent While it is easy to dissolve the above-mentioned hydrophobing processing agent in a supercritical carbon dioxide and a gas-liquid interface does not occur within a supercritical drying container And the reaction by-product generated at the hydrophobing processing reaction using the above-mentioned hydrophobing processing agent is alcohol, and is what is similarly dissolved in a supercritical carbon dioxide. Without it seeming that the hydrophobing processing agent and reaction by-product which remain in a gel compound have a bad influence on a gel compound at the time of supercritical drying While being able to skip the process which washes the gel compound after hydrophobing processing with a solvent, being able to shorten process time amount and being able to raise the effectiveness of productivity, the amount of the solvent used can be minimum-ized and a production cost can be made cheap.

[0057] Moreover, since invention of claim 4 sets the gel compound which carried out hydrophobing processing in a supercritical drying container and was made to carry out supercritical drying of the gel compound, without being filled up with a solvent in a supercritical drying container, the need of it that a lot of solvents and carbon dioxides in a supercritical drying container are permuted at the time of supercritical drying is lost like [ in the case of being filled

up with a solvent in a supercritical drying container, and setting a gel compound ], and it can perform supercritical drying efficiently.

[0058] Moreover, since invention of claim 5 changes a hydrophobing processing solution into an acid condition and was made to carry out hydrophobing processing of the gel compound under acid conditions, it can raise the reactivity of a hydrophobing processing agent and can perform hydrophobing processing efficiently.

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**TECHNICAL FIELD**

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[Field of the Invention] It is related with the manufacture approach of aerogel of the rate of optical refraction having been low, and having excelled in hydrophobicity while this invention was excellent in adiathermic and light transmission nature.

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PRIOR ART

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[Description of the Prior Art] The silica aerogel useful as a heat insulator which has translucency is offered from the former. As a process of this aerogel, an ARUKOSHI xylan is hydrolyzed and the approach of drying the gel compound obtained by carrying out condensation polymerization of this on the supercritical conditions more than the critical point of this dispersion medium under existence of a dispersion medium is learned as indicated by the U.S. Pat. No. 4402927 official report, the U.S. Pat. No. 4432956 official report, and the U.S. Pat. No. 4610863 official report.

[0003] In these approaches, organic solvents, such as a carbon dioxide or ethanol, are used as a dispersion medium at the time of supercritical drying. However, the high silanol group of a hydrophilic property is formed of the moisture to which hygroscopicity was discovered since it had the silanol group on the front face, and it was easy to adsorb the moisture in an ambient atmosphere, and stuck further, the aerogel obtained by carrying out supercritical drying, using a carbon dioxide as a dispersion medium passes through the moisture in an ambient atmosphere, and it much more becomes easy to stick with the time to it. Moreover, about the aerogel obtained by carrying out supercritical drying, using organic solvents, such as ethanol, as a dispersion medium, since it has the alkoxyl group on the front face, although it has hydrophobicity immediately after supercritical drying, the moisture of an ambient atmosphere hydrolyzes with time, a silanol group is formed in that result table side, and this alkoxyl group comes to adsorb the moisture in an ambient atmosphere similarly.

[0004] And when aerogel adsorbed moisture in this way, it was what the problem that a property optical [adiathermic / translucency, adiathermic, etc. / that] and thermal will fall, and change and the crack of a dimension will arise with the contraction which originates in adsorption of this moisture further, will cause degradation of quality or the engine performance these results, and practicality will be missing generates.

[0005] Then, in order that this invention person etc. may conquer the fault by the water adsorption of this aerogel, After carrying out hydrophobing processing of the gel compound which obtained alkoxysilane and a sodium silicate as a raw material in a liquid solvent, by performing supercritical drying the approach (JP,5-279011,A —) of obtaining the aerogel made into hydrophobicity refer to Japanese Patent Application No. No. 342176 [eight to] — or by adding a hydrophobing processing agent in a supercritical drying container at the time of supercritical drying, and performing hydrophobing processing in the state of supercritical The approach (refer to JP,7-138375,A and Japanese Patent Application No. No. 343282 [eight to]) of obtaining the aerogel made into hydrophobicity is proposed. Thus, by carrying out hydrophobing processing of the aerogel, the aerogel in which a property does not deteriorate with time by adsorption of moisture can be obtained.

[0006] In carrying out hydrophobing processing of the gel compound as mentioned above, and manufacturing hydrophobic aerogel, he uses a solvent before hydrophobing processing and is trying to wash a gel compound beforehand conventionally here. This is for preventing the moisture contained in the gel compound after gelation reacting with a hydrophobing processing agent, and reducing the reaction effectiveness of a hydrophobing processing agent.

[0007] Moreover, in order to remove the reaction by-product generated by the hydrophobing



processing agent which remains in a gel compound after hydrophobing processing, or hydrophobing processing, he uses a solvent similarly and is trying to wash a gel compound. If the concentration of the hexamethyldisilazane which remains in the gel compound after hydrophobing processing is more than solubility to the inside of the carbon dioxide of the dispersion medium of supercritical drying when hexamethyldisilazane is used as for example, a hydrophobing processing agent, this In the supercritical drying process after hydrophobing processing, a gas-liquid interface arises within a desiccation container. The problem that the structure of a gel compound will be destroyed as a result arises, or Or it is for preventing that the problem that an ammonium carbonate deposits [ the ammonia generated as a reaction by-product by hydrophobing processing ] in response to the time of supercritical drying with a carbon dioxide, and this blocks piping of supercritical drying equipment arises.

[0008] Moreover, in case the gel compound which carried out hydrophobing processing is set in a desiccation container in a supercritical drying process, he is trying to fill up solvents, such as alcohol, with the manufacturing method of conventional hydrophobic aerogel beforehand in a desiccation container. In case this sets a gel compound in a desiccation container, it is for preventing a gel compound's drying and a crack occurring.

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EFFECT OF THE INVENTION

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[Effect of the Invention] The manufacture approach of the hydrophobic aerogel which starts claim 1 of this invention as mentioned above While hydrolyzing an alkoxysilane compound, after carrying out condensation polymerization, preparing a gel compound and carrying out hydrophobing processing of this gel compound, by carrying out supercritical drying After preparing the above-mentioned gel compound under existence of alcohol in manufacturing hydrophobic aerogel and the gel compound has contained water, without washing a gel compound with a solvent Hydrophobing processing of this gel compound is carried out in the hydrophobing processing solution containing the organic silane compound which has an alkyl group and an alkoxyl group. Subsequently, since the solvent contained in this gel compound that carried out hydrophobing processing is permuted by the carbon dioxide and it was made to carry out supercritical drying of the gel compound after this Alcohol is contained in the gel compound of an alkoxysilane compound. It is what can be made to be able to dissolve water and a hydrophobing processing agent in this alcohol, and can perform hydrophobing processing. And the hydrophobing processing agent which consists of an organic silane compound which has an alkyl group and an alkoxyl group Will hydrolyze, if moisture exists in a gel compound, and an alkoxyl group replaces a hydroxyl group. It is what becomes easy to react with the hydroxyl group on the front face of pore of a gel compound, and can carry out hydrophobing processing of the gel compound. Consequently, a solvent does not need to wash a gel compound and hydrophobing processing can be performed in the condition [ that moisture has been included in the gel compound ]. While the process which washes a gel compound with a solvent can become unnecessary, can shorten process time amount and can raise the effectiveness of productivity, the amount of the solvent used can be minimum-ized and a production cost can be made cheap. [0055] Moreover, since invention of claim 2 was made to carry out supercritical drying of the gel compound in above-mentioned claim 1, without washing a gel compound with a solvent after carrying out hydrophobing processing of the gel compound While it is easy to dissolve the above-mentioned hydrophobing processing agent in a supercritical carbon dioxide and a gas-liquid interface does not occur within a supercritical drying container And the reaction by-product generated at the hydrophobing processing reaction using the above-mentioned hydrophobing processing agent is alcohol, and is what is similarly dissolved in a supercritical carbon dioxide. Without it seeming that the hydrophobing processing agent and reaction by-product which remain in a gel compound have a bad influence on a gel compound at the time of supercritical drying While being able to skip the process which washes the gel compound after hydrophobing processing with a solvent, being able to shorten process time amount and being able to raise the effectiveness of productivity, the amount of the solvent used can be minimum-ized and a production cost can be made cheap.

[0056] The manufacture approach of the hydrophobic aerogel concerning claim 3 of this invention After preparing a gel compound and carrying out hydrophobing processing of this gel compound by making a sodium silicate gel, by carrying out supercritical drying In manufacturing hydrophobic aerogel, hydrophobing processing is carried out in the hydrophobing processing solution containing the organic silane compound which has an alkyl group and an alkoxyl group for the above-mentioned gel compound. Next, since the solvent contained in a gel compound is

permuted by the carbon dioxide and it was made to carry out supercritical drying of the gel compound after this, without washing a gel compound with a solvent While it is easy to dissolve the above-mentioned hydrophobing processing agent in a supercritical carbon dioxide and a gas-liquid interface does not occur within a supercritical drying container And the reaction by-product generated at the hydrophobing processing reaction using the above-mentioned hydrophobing processing agent is alcohol, and is what is similarly dissolved in a supercritical carbon dioxide. Without it seeming that the hydrophobing processing agent and reaction by-product which remain in a gel compound have a bad influence on a gel compound at the time of supercritical drying While being able to skip the process which washes the gel compound after hydrophobing processing with a solvent, being able to shorten process time amount and being able to raise the effectiveness of productivity, the amount of the solvent used can be minimum-ized and a production cost can be made cheap.

[0057] Moreover, since invention of claim 4 sets the gel compound which carried out hydrophobing processing in a supercritical drying container and was made to carry out supercritical drying of the gel compound, without being filled up with a solvent in a supercritical drying container, the need of it that a lot of solvents and carbon dioxides in a supercritical drying container are permuted at the time of supercritical drying is lost like [ in the case of being filled up with a solvent in a supercritical drying container, and setting a gel compound ], and it can perform supercritical drying efficiently.

[0058] Moreover, since invention of claim 5 changes a hydrophobing processing solution into an acid condition and was made to carry out hydrophobing processing of the gel compound under acid conditions, it can raise the reactivity of a hydrophobing processing agent and can perform hydrophobing processing efficiently.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] As mentioned above, while the manufacturing method of conventional hydrophobic aerogel took the process time amount of washing since a solvent was used for a hydrophobing processing front and the back for a gel compound and he was trying to wash, and productive efficiency became very low, it was what the amount of the solvent used becomes great and has a problem also in respect of a production cost. Moreover, since it is filled up with a solvent in the container of supercritical drying and he is trying to set a gel compound If it has a problem in the production cost by use of a solvent, it is filled up with a solvent in a supercritical drying container still in this way and a gel compound is set while the injection time of a solvent is required similarly and productive efficiency becomes low Since it filled up with the solvent also around the gel compound in the supercritical drying container, the time amount taken to permute the solvent in a supercritical drying container with a carbon dioxide at the time of supercritical drying became long, and productive efficiency was what becomes still lower.

[0010] It aims at offering the manufacture approach of the hydrophobic aerogel which this invention is made in view of the above-mentioned point, and can shorten process time amount, and can raise the effectiveness of productivity, and can minimum-ize the amount of the solvent used, and can make a production cost cheap.

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MEANS

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[Means for Solving the Problem] The manufacture approach of the hydrophobic aerogel concerning claim 1 of this invention While hydrolyzing an alkoxysilane compound, after carrying out condensation polymerization, preparing a gel compound and carrying out hydrophobing processing of this gel compound, by carrying out supercritical drying After preparing the above-mentioned gel compound under existence of alcohol in manufacturing hydrophobic aerogel and the gel compound has contained water, without washing a gel compound with a solvent Hydrophobing processing of this gel compound is carried out in the hydrophobing processing solution containing the organic silane compound which has an alkyl group and an alkoxyl group. Subsequently, the solvent contained in this gel compound that carried out hydrophobing processing is permuted by the carbon dioxide, and it is characterized by carrying out supercritical drying of the gel compound after this.

[0012] Moreover, invention of claim 2 is characterized by carrying out supercritical drying of the gel compound in above-mentioned claim 1, without washing a gel compound with a solvent, after carrying out hydrophobing processing of the gel compound.

[0013] The manufacture approach of the hydrophobic aerogel concerning claim 3 of this invention After preparing a gel compound and carrying out hydrophobing processing of this gel compound by making a sodium silicate gel, by carrying out supercritical drying In manufacturing hydrophobic aerogel, hydrophobing processing is carried out in the hydrophobing processing solution containing the organic silane compound which has an alkyl group and an alkoxyl group for the above-mentioned gel compound. Next, without washing a gel compound with a solvent, the solvent contained in a gel compound is permuted by the carbon dioxide, and it is characterized by carrying out supercritical drying of the gel compound after this.

[0014] Moreover, in above-mentioned claim 1 thru/or 3, without being filled up with a solvent in a supercritical drying container, invention of claim 4 sets the gel compound which carried out hydrophobing processing in a supercritical drying container, and is characterized by carrying out supercritical drying of the gel compound.

[0015] Moreover, invention of claim 5 is characterized by changing a hydrophobing processing solution into an acid condition, and carrying out hydrophobing processing of the gel compound under acid conditions in above-mentioned claim 1 thru/or 4.

[0016] Moreover, invention of claim 6 is characterized by using dimethyldimethoxysilane as an organic silane compound in above-mentioned claim 1 thru/or 5.

[0017]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained.

[0018] Generally as a silica raw material for obtaining aerogel, alkoxysilane and a sodium silicate (water glass) are used. As alkoxysilane, 2 organic-functions alkoxysilane, 3 organic-functions alkoxysilane, There is 4 organic-functions alkoxysilane. As 2 organic-functions alkoxysilane Dimethyldimethoxysilane, Dimethyl diethoxysilane, diphenyl diethoxysilane, diphenyldimethoxysilane, Methylphenyl diethoxysilane, methylphenyl dimethoxysilane, As 3 organic-functions alkoxysilane, diethyldiethoxysilane, diethyldimethoxysilane, etc. Methyl trimethoxysilane, Methyl triethoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, Phenyltrimethoxysilane, a phenyl TORIETOSHI xylan, etc. can be mentioned for a tetramethoxy

silane, a tetra-ethoxy silane, etc. as 4 organic-functions alkoxysilane, respectively.

[0019] And by mixing with the solvent which has compatibility for this alkoxysilane in water and water, and dissolves alkoxysilane, and mixing this mixed solution, hydrolysis and condensation polymerization advance and a gel compound can be obtained. By this invention, alcohol, such as a methanol, ethanol, isopropanol, and a butanol, is used as this solvent.

[0020] Moreover, about a sodium silicate, a gel compound can be obtained by making a solution into a supersaturation condition, depositing a silicon oxide, and making it gel by adjusting pH of a sodium-silicate solution (water glass solution) near neutrality.

[0021] Next, hydrophobing down stream processing which carries out hydrophobing of the gel compound prepared as mentioned above is explained. Hydrophobing processing is performed in order to make the hydroxyl group of the silanol group which a gel compound has react with the functional group which a hydrophobing processing agent has and to carry out hydrophobing. Although especially the technique of performing hydrophobing processing is not limited, after being immersed, agitating a gel compound for example, in the hydrophobing processing solution made to dissolve a hydrophobing processing agent in a solvent and making a hydrophobing processing agent permeate in a gel compound, it heats if needed, and the method of making a hydrophobing processing reaction perform is mentioned.

[0022] While dissolving easily using the organic silane compound which has an alkyl group and an alkoxyl group as a hydrophobing processing agent in this invention here into the carbon dioxide used as a solvent in the case of supercritical drying, it is desirable to use what also dissolves the by-product produced in the case of a hydrophobing processing reaction into a carbon dioxide. As such a hydrophobing processing agent, trimethylmethoxysilane, dimethyldimethoxysilane, methyl trimethoxysilane, ethyltrimethoxysilane, trimethylethoxysilane, dimethyl diethoxysilane, methyl triethoxysilane, etc. can be mentioned, for example.

[0023] Thus, when it consists of an alkyl group and an alkoxyl group and moisture exists in the gel compound before hydrophobing processing, a hydrophobing processing agent is hydrolyzed, an alkoxyl group replaces a hydroxyl group and a hydrophobing processing agent becomes easy to react with the hydroxyl group on the front face of pore of a gel compound. Although the above-mentioned hydrophobing processing agent has low reactivity compared with the hexamethyldisilazane generally used as a hydrophobing processing agent, when moisture exists in a gel compound, reactivity increases.

[0024] Here, when a sodium silicate is used as a silica raw material, the gel compound after gelation is obtained in the state of the condition, i.e., a hydrogel, that the interior is filled up with water. Since the above-mentioned hydrophobing processing agent cannot melt into water easily, it is desirable that solvents, such as water and alcohol made to dissolve a hydrophobing processing agent mutually, wash a gel compound in advance of hydrophobing processing in this case.

[0025] As a solvent, on the other hand, since gelation was processed for alcohol when alkoxysilane was used as a silica raw material, the interior of a gel compound will be able to be filled up with alcohol with water, and water and a hydrophobing processing agent can be dissolved in this alcohol. Therefore, when it is made to gel in alcohol, using alkoxysilane as a silica raw material, although a solvent washes a gel compound, it is unnecessary, and hydrophobing processing can be performed in the condition [ that moisture has been included in the gel compound ].

[0026] Moreover, an acid is added, it changes into an acid condition, and you may make it raise the reactivity of a hydrophobing processing agent under acid conditions into a hydrophobing processing solution in this hydrophobing down stream processing. It is desirable to change into an acid condition as [ become / a pH value / as an acid to add, can mention organic acids, such as inorganic acids, such as a hydrochloric acid and a sulfuric acid, and an acetic acid, oxalic acid, here, and / the range of 4-6 ].

[0027] As a solvent used in order to dissolve the above-mentioned hydrophobing processing agent, with the solvent which a hydrophobing processing agent dissolves easily and the gel compound before hydrophobing processing contains although alcohols, such as a methanol, ethanol, and isopropanol, a xylene, toluene, benzene, N.N-dimethylformamide, etc. can be

mentioned, if replaceable, it will not be limited to these things, for example.

[0028] Next, the process which carries out supercritical drying of the gel compound which performed hydrophobing processing as mentioned above is explained. Supercritical drying is the drying method for removing a solvent (dispersion medium) from the critical point or the critical point of a solvent included in the gel compound gradually in the supercritical ambient atmosphere of elevated-temperature high pressure. Although there is also the approach of drying under these supercritical conditions using a methanol, ethanol, etc. as this solvent, since critical temperature is very high in this case, from fields, such as safety, to carrying out industrially, it is not desirable. For this reason, he is trying to use a carbon dioxide with critical temperature low as a solvent (dispersion medium) in this invention.

[0029] And after permuting all or some of solvents with which it is immersed into the liquefaction carbon dioxide of 50 - 60 atmospheric-pressure extent, and a gel compound contains a gel compound, for example by the liquefaction carbon dioxide with the critical point lower than this solvent in carrying out supercritical drying of the gel compound which performed the above-mentioned hydrophobing processing in this invention, it can dry under the supercritical conditions of the independent system of a carbon dioxide, or the mixed stock of a carbon dioxide and a solvent.

[0030] Here, in order to be easy to dissolve in a supercritical carbon dioxide and to dissolve in infinity in a supercritical drying process above predetermined temperature and a flow and pressure requirement further, a gas-liquid interface does not generate the above-mentioned hydrophobing processing agent used in this invention within a supercritical drying container. And at the hydrophobing processing reaction using the above-mentioned hydrophobing processing agent, since the reaction by-product generated is also alcohol, it dissolves in a supercritical carbon dioxide similarly. Even if it skips the process which washes the gel compound after hydrophobing processing with a solvent, the hydrophobing processing agent or reaction by-product which remain in a gel compound do not have a bad influence on a gel compound at the time of supercritical drying, and it becomes unnecessary therefore, for a solvent to wash the gel compound after hydrophobing processing.

[0031] Moreover, in setting a gel compound in a supercritical drying container, in a supercritical drying process, a gel compound can be set in the condition of not being beforehand filled up with the solvent in a supercritical drying container. In this case, although there is a possibility that a crack may occur by desiccation of a gel compound, when it is not necessary to make an issue of debasement especially by generating of a crack, it may be made to set a gel compound in the condition of not being beforehand filled up with the solvent in a supercritical drying container. Therefore, the need that a lot of solvents and carbon dioxides in a supercritical drying container are permuted at the time of supercritical drying is lost like [ in the case of being filled up with a solvent in a supercritical drying container, and setting a gel compound ], a gel compound is only set in a supercritical drying container, supercritical drying can be performed, and supercritical drying can be performed efficiently.

[0032] In addition, although not limited especially about the configuration of the gel compound with which hydrophobing processing and supercritical drying are presented, since the drying efficiency of a gel compound can be raised and particle size of a gel compound can be made [ and ] small by carrying out like [ thing / tabular ] the shape of a bead, or the letter of grinding, it is much more hard coming to generate the crack by the desiccation at the time of setting a gel compound in a supercritical drying container.

[0033] By carrying out hydrophobing processing and carrying out supercritical drying of the gel compound further as mentioned above, the outstanding hydrophobicity is given and the silica aerogel which has high translucency can be obtained. That is, the hydroxyl group of the silanol group which exists in the silica front face of aerogel is permuted by hydrophobing processing by the hydrophobic group of a hydrophobing processing agent, adsorbing the moisture in an ambient atmosphere of the aerogel obtained is lost, and the fall of the property with time by water absorption of it is lost. And in case it can dry without the phase transition of the solvent in a gel compound, i.e., the so-called evaporation and condensation, happening and a solvent is removed by supercritical drying, it can control the structure of a gel compound being destroyed or

condensing, and the aerogel obtained by supercritical drying will become porosity. And this aerogel is the structure which consists of a very detailed silica particle, and as for that particle diameter, far smaller than the wavelength of light, although its space between particles is smaller [ than the mean free path of air ] uniform, and its thermal conductivity is small and it is a porous body, it has translucency.

[0034] The aerogel concerning this invention obtained as mentioned above is useful for applications, such as a heat insulator in opening, an acoustic material, the Cherenkov component, and catalyst support.

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EXAMPLE

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[Example] Next, an example explains this invention concretely.

[0036] (Example 1) After slushing into the container the sol obtained by blending 47 weight sections and a methanol in the 163 weight sections, blending 50 weight sections and 15-N aqueous ammonia for water at a rate of 1 weight section, and agitating the oligomer (the "methyl silicate 51" by COL coat incorporated company, average molecular weight 470 [ about ]) of a tetramethoxy run for about 30 seconds and making this sol gel, it was left at the room temperature on the 1st, and the gel compound was obtained. Thus, the obtained gel compound was ground and the particle whose mean particle diameter is about 3mm was produced.

[0037] Next, as a hydrophobing processing solution, the isopropanol solution of the dimethyldimethoxysilane (reagent by Dow Corning Toray Silicone, Inc.) of 0.6 mol/L was prepared, and concentration was immersed in this hydrophobing processing solution in the gel compound of the shape of a particle produced as mentioned above, and performed hydrophobing processing for three days at the room temperature. At this time, it set up so that the volume of a hydrophobing processing solution and the volume of a gel compound might become equal, and the hydrophobing processing solution was agitated several times on the 1st.

[0038] Next, hydrophobic aerogel was obtained by putting the gel compound which carried out hydrophobing processing in this way into a supercritical container, making the inside of a supercritical drying container into 80 degrees C and 160 atmospheric pressures which are the supercritical conditions of a carbon dioxide, using a carbon dioxide as a solvent (dispersion medium), and performing supercritical drying for 5 hours.

[0039] (Example 2) In the example 1, the methanol was used instead of isopropanol as a solvent for dissolving a hydrophobing processing agent, and the hydrophobing processing solution was prepared. Others obtained hydrophobic aerogel like the example 1.

[0040] (Example 3) In the example 1, into the hydrophobing processing solution, it adds 2% and dilute hydrochloric acid was used by the volume. Others obtained hydrophobic aerogel like the example 1.

[0041] (Example 4) In the example 1, methyl trimetoxysilane (reagent by Dow Corning Toray Silicone, Inc.) was used instead of dimethyldimethoxysilane as a hydrophobing processing agent, and the hydrophobing processing solution was prepared. Others obtained hydrophobic aerogel like the example 1.

[0042] (Example 5) In setting the gel compound which performed hydrophobing processing in a supercritical drying container, in the example 1, it was beforehand filled up with isopropanol in the supercritical drying container. Others obtained hydrophobic aerogel like the example 1.

[0043] (Example 6) The inside of the column with which ion-exchange resin ("Amberlite IR-120B" by ORGANO CORP.) was filled up with the hydrosol solution which mixed the sodium-silicate water solution (the "J sodium silicate No. 3" by Nippon Chemical Industrial Co., Ltd.) in 10 weight sections, mixed ion exchange water at a rate of 32 weight sections, and was prepared was passed. At this time, the ratio of the number of mols of the sodium atom in a hydrosol solution and the exchangeable number of mols of ion exchange resin was 0.5. Moreover, pH of the hydrosol solution obtained by passing ion exchange resin was 3. Next, 1 weight section addition of the aqueous ammonia of concentration was carried out 2.8% of the weight at this

hydrosol solution 200 weight section, and it agitated quickly. pH of the hydrosol solution at this time was 6. This hydrosol solution was put at the room temperature on the 1st, and the hydrogel was obtained. The obtained gel compound was ground and the particle whose mean particle diameter is 3mm was produced.

[0044] It was immersed in the isopropanol of this volume and the particle of the obtained gel compound was permuted by the water in a gel compound. This permutation actuation was performed a total of 4 times. And the rest carried out hydrophobing processing like the example 1, carried out supercritical drying further, and obtained hydrophobic aerogel.

[0045] (Example 1 of a comparison) In the example 1, before carrying out hydrophobing processing, isopropanol was used, the gel compound was washed twice, and also after hydrophobing processing, isopropanol was used and the gel compound was washed twice. Others obtained hydrophobic aerogel like the example 1. At this time, washing of a gel compound required the day per washing.

[0046] (Example 2 of a comparison) In the example 1 of a comparison, hexamethyldisilazane (reagent by Dow Corning Toray Silicone, Inc.) was used instead of dimethyldimethoxysilane as a hydrophobing processing agent, and the hydrophobing processing solution was prepared. Others obtained hydrophobic aerogel like the example 1 of a comparison.

[0047] (Example 3 of a comparison) In the example 1, hexamethyldisilazane (reagent by Dow Corning Toray Silicone, Inc.) was used instead of dimethyldimethoxysilane as a hydrophobing processing agent, and the hydrophobing processing solution was prepared. Others obtained hydrophobic aerogel like the example 1.

[0048] (Example 4 of a comparison) In the example 1, it was made not to perform hydrophobing processing and aerogel was obtained like the example 1.

[0049] The silica raw material in above-mentioned examples 1-6 and examples 1-4 of a comparison, the class of hydrophobing processing agent, The class of solvent of a hydrophobing processing solution, pH of a hydrophobing processing solution, the bath ratio of a gel compound and a hydrophobing processing solution, The days which the existence of restoration of the solvent to the count of washing before hydrophobing processing, the count of washing after hydrophobing processing, and the supercritical drying container in the case of supercritical drying and the amount of the solvent used per 1l. of gel compounds, and hydrophobing down stream processing took are shown in Table 1.

[0050]

[Table 1]

	silica 原料	疎水化処理剤	溶媒	処理液 のpH	ゲルと溶液 の溶比	疎水化前 洗浄回数	疎水化後 洗浄回数	超臨界乾燥 時の溶媒 充填の有無	ゲル1L当り の溶媒 使用量 (L)	疎水化 処理工程 日数 (日)
実施例1	メチルシラン-151	ジメチルジメトキシシラン	イソプロパノール	7	0.5	0	0	なし	1	3
実施例2	メチルシラン-151	ジメチルジメトキシシラン	メタノール	7	0.5	0	0	なし	1	3
実施例3	メチルシラン-151	ジメチルジメトキシシラン	イソプロパノール	5	0.5	0	0	なし	1	3
実施例4	メチルシラン-151	メチルトリメトキシシラン	イソプロパノール	7	0.5	0	0	なし	1	3
実施例5	メチルシラン-151	ジメチルジメトキシシラン	イソプロパノール	7	0.5	0	0	あり	2	3
実施例6	ケイ酸ソーダ	ジメチルジメトキシシラン	イソプロパノール	7	0.5	4	0	なし	5	3
比較例1	メチルシラン-151	ジメチルジメトキシシラン	イソプロパノール	7	0.5	2	2	あり	6	7
比較例2	メチルシラン-151	ヘキサメチルジシラザン	イソプロパノール	7	0.5	2	2	あり	6	7
比較例3	メチルシラン-151	ヘキサメチルジシラザン	イソプロパノール	7	0.5	0	0	なし	1	3
比較例4	メチルシラン-151	—	—	—	—	0	0	なし	0	0

[0051] Next, the bulk density of aerogel after the humidity resistance test which exposes aerogel immediately after supercritical drying for 48 hours into the ambient atmosphere of the temperature of 60 degrees C and 90% of humidity RH, thermal conductivity, and light transmittance were measured about the aerogel obtained as mentioned above in examples 1-5

and the examples 1-4 of a comparison. The thermal conductivity measuring apparatus by the stationary method by Hidehiro energy machine incorporated company was used for thermal conductivity here, and it is an approach based on ASTM-C518, and measured on the laying temperature of 20 degrees C, and 40-degree C conditions. Moreover, about light transmittance, it asked by measuring the illuminance before and behind installation of the sample produced in thickness of 12mm by aerogel by making a fluorescent lamp into the light source all over the acrylic box using an illuminometer (illuminometer by YOKOGAWA instrument incorporated company "a part number 510-02"). These results are shown in Table 2.

[0052]

[Table 2]

	かさ密度 (g/cm <sup>3</sup> )		熱伝導率 (W/mK)		光透過率 (%)	
	超臨界乾燥後	耐湿試験後	超臨界乾燥後	耐湿試験後	超臨界乾燥後	耐湿試験後
実施例1	0.11	0.11	0.019	0.020	86	86
実施例2	0.12	0.12	0.020	0.020	85	85
実施例3	0.12	0.12	0.019	0.019	84	84
実施例4	0.12	0.13	0.020	0.020	85	86
実施例5	0.11	0.11	0.020	0.021	87	86
実施例6	0.11	0.12	0.020	0.021	83	84
比較例1	0.11	0.12	0.020	0.021	87	85
比較例2	0.12	0.12	0.019	0.019	86	86
比較例3	0.14	0.15	0.021	0.022	73	70
比較例4	0.11	0.37	0.020	0.350	87	38

[0053] It is checked that the example 6 which does not perform washing after the examples 1-5 which do not perform washing hydrophobing processing before or after hydrophobing processing, and hydrophobing processing also has damp-proof ability equivalent to the thing of the examples 1 and 2 of a comparison which performs washing hydrophobing processing before and after hydrophobing processing so that it may see in Table 2.

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[Translation done.]